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Experience from the Use of Tenax in Distributed Ambient Air Volume Sets

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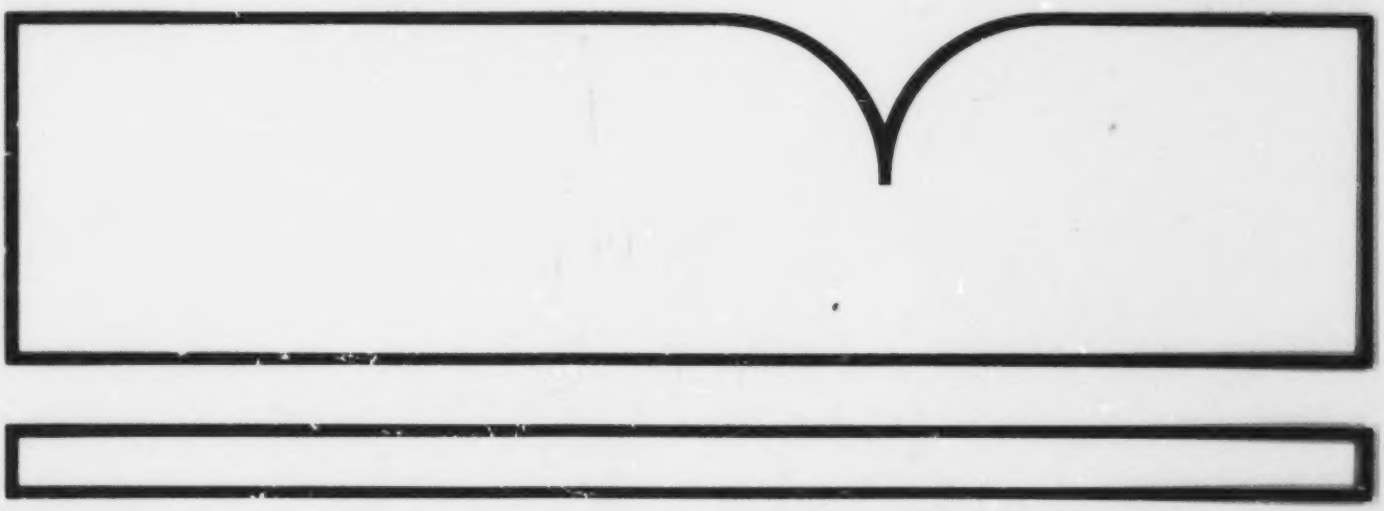

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EXPERIENCE FROM THE USE OF TENAX IN DISTRIBUTED AMBIENT AIR VOLUME SETS

by

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16. ABSTRACT

Solid adsorbent beds are a practical, commonly used way to concentrate organic molecules from large volumes of air to make analysis possible. A small set of such beds exposed simultaneously, but each at a quite different flow rate, has been suggested as a way to assess the presence of complications.

This sampling approach represents a strong quality assurance activity because it provides a summary index of the effects of a sizable number of variables to aid in quality assessment. Implementation is quite practical. Costs are not trivial since sets of four samples are preferred. However, some complications easily discovered but not specifically identifiable by this approach might elude more conventional quality control checking. Examples would be selective contamination, inadequate retention and artifact reactions. Results Results from tandem tube and non-tandem tube sets are presented to illustrate these suggestions.

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Solid adsorbent beds are a practical, commonly used way to concentrate organic molecules from large volumes of air to make analysis possible. A small set of such beds exposed simultaneously, but each at a quite different flow rate, has been suggested as a way to assess the presence of complications. Many kinds of complications, e.g., leakage during sampling, artifact formation, contamination, inadequate retention, transcription errors, calibration curve errors, will be revealed if present and important by destroying the expected constancy of the apparent concentration within the set. No enumeration or identification of the complications is possible from the data set alone. Neither will any complication which scales linearly with air volume, e.g., a poor but constant recovery, show any effect.

This sampling approach represents a strong quality assurance activity because it provides a summary index of the effects of a sizable number of variables to aid in quality assessment. Implementation is quite practical. Costs are not trivial since sets of four samples are preferred. However, some complications easily discovered but not specifically identifiable by this approach might elude more conventional quality control checking. Examples would be selective contamination, inadequate retention and artifact reactions. Results from tandem tube and non-tandem tube sets are presented to illustrate these suggestions.

EXPERIENCE FROM THE USE OF TENAX IN DISTRIBUTED AMBIENT AIR VOLUME SETS

Introduction

Solid adsorbents have been used for many years to selectively concentrate trace contaminants in air to provide sufficient material for analysis. The technique is quite convenient to apply in the field but quality assurance is difficult. The usual quality control activities, e.g., the need to check flow calibrations and sample handling/installation at a perhaps distant field site and the usual challenges presented to the analytical laboratory, continue to be useful. In addition, however, there are special complications with adsorbents about which relatively little is known and which cannot be assessed easily by the usual checks. For example, adequacy of retention is an important question particularly when some of the polymeric adsorbents with modest retention volumes are utilized. Retention volumes are functions of temperature, composition, and to some extent bed geometry/flow rate parameters.[1] Chemical reactions on the surface during sampling and desorption are also very problematic and largely shrouded in ignorance at present.[2]

A practical situation-specific approach to obtain a synoptic view of the combined effects of many of these possibilities has been proposed.[3] Costs are not insignificant and enumeration or identification of complications cannot be done from such data alone. However, such situation-specific synoptic indexes can be quite useful in evaluating data quality. The remainder of this paper presents a brief description of the approach and the results from some ambient sampling where it has been applied.

Experimental

Distributed Air Volume Sampling

This approach to sampling will be outlined only briefly here for completeness since it has been discussed elsewhere.[3] Several (at present usually four) samples are exposed simultaneously (i.e., same starting and stopping time[3]) in the same parcel of air. However, each tube samples a very different air volume by using a different flow rate. Results from such a set are simply sorted into a group where the apparent concentrations are a function of the volume sampled and a second group where they are not. The second group is the subset representing the best estimate of the trace substances presumably in the air when the given adsorbent is used for sampling. The first group is the subset affected by some complication.[3] These data require selection or correction (if possible) before they can be used to make any estimate of the atmospheric composition.

Sampling

Sampling was done with solvent cleaned and thermally desorbed Tenax.[4] About 1.2 g in beds 1.5 cm in diameter and 6 cm long were held in glass or stainless tubes using plugs of cleaned glass wool. Prepared cartridges were placed in cleaned glass culture tubes which were in turn sealed in metal cans with compression lids and then shipped to a sampling site. During sampling cartridges hung vertically from fittings which led to calibrated mass flow controllers and a pump. Flow rates ranged between 10 and 480 cm^3/min over the course of several investigations. Field quality assurance requires a leak test and independent verification of flow rates at the beginning and end of each sampling period. Independent audits are also done occasionally.

Analysis

Thermal desorption of Tenax and cryofocusing onto a 50 m WCOT (SE-30) glass capillary was followed by detection in a Finnigan 4021 mass spectrometer.[5] Data were interpreted by a reverse search using the expected retention time as the primary selection variable. Further qualitative identification was done in a fully automated manner by requiring acceptable ratios of certain functions routinely produced by the INCOS data system. Failure to identify a substance sought in this manner does not guarantee its absence. Manual verification is required for that but is not done routinely.

Calibration of the spectrometer was done by direct splitless injection of gaseous mixtures of 20 to 35 substances each[6] with the septum sweep gas also being led to the column. Quadratic calibration curves and detection limits were generated in a completely automated way and applied automatically to acceptably identified substances.

Quality assurance requires the successful analysis each day of (1) a direct injection of a gaseous mixture of 35 compounds to test calibration and tuning, (2) a Grob mixture to assess chromatographic column function, (3) quantitative recovery of a standard placed on each sample just prior to desorption to test adequacy of transfer, and (4) an order of sample analysis unrelated to order of sample collection. External audits using Tenax cartridges doped with standards are also done each day of operation.

Results and Discussion

Results from several experiments with and without tandem tubes in the sets are summarized in Tables II through IV. Before beginning a discussion of them, the hypothetical data in Table I can illustrate the necessarily equivocal evaluations based solely on data from a single set and the implications of this approach for quality assurance.

TABLE I. HYPOTHETICAL DATA SET FOR ONE SUBSTANCE

Air Volume, liters	10	20	40	80
Amount, ng	50	80	140	260
Apparent Conc. $\mu g/m^3$	5	4	3.5	3.3

The following possibilities need to be considered assuming that the expected maximum difference between any two results should be 1 $\mu g/m^3$. Using this yardstick some complication exists with this set. It might be some or any of the following or even others (e.g., clerical) which are conceivable:

a. Artifact reactions have occurred.

b. Loss of material has occurred because the true retention volume was exceeded. Retention volumes are functions of bed design, flow, temperature and gas composition.

c. The flow rate was misread or mis-set in a consistent way. If all integrated air volumes are increased by 7 liters and the amount of material found is accepted as stated, the apparent concentrations are equal.

d. The flow meters have been miscalibrated.

e. The analytical detector has been miscalibrated. Note that a subtraction of 20 ng from each analytical result yields equal apparent concentrations if the air volumes are accepted as stated.

f. The 10-liter sample had an unusually high blank value which was not suspected.

g. The 10-liter sample was contaminated. Contamination can be isolated and selective and need not include all components on a given cartridge or all cartridges within a shipment.

Clearly, use of only four apparent concentrations is insufficient to distinguish among just these seven selected possibilities. Equally clearly, other usual quality assurance practices can help to eliminate or select items c through e. A view of all results from a set may also help to eliminate or favor certain possibilities. However, possibilities a, b, f and g will generally remain troublesome. Sometimes doping the tube with isotopically altered molecules of interest can be done to check b. But, quantitative recovery of labeled material does not imply absence of artifact reactions, blank or contamination problems. Distributed air volume sets then can facilitate identification of presumably corrupted data not describing the atmosphere sampled when causes seem likely to elude detection by usual quality checks. But, they cannot identify the complications.

Turning now to the data in Tables II - IV, independent evidence for possibilities c - e above was absent in every case. All other possibilities remain open. All data were obtained by the same personnel and procedures. However, seasons and locations differ in each Table. For all substances except benzene and methylbenzene it has been estimated that 95% of the results below 10 $\mu g/m^3$ should differ by no more than 1 $\mu g/m^3$. For benzene and methylbenzene results should differ by no more than 2 $\mu g/m^3$. For concentrations above 10 $\mu g/m^3$ the criteria are 10% and 20%, respectively.[3]

Table II contains a set which behaves in essentially a textbook fashion. Duplicate tandem tubes were exposed at each of four flow rates. Nothing in excess of the blank values was found on any of the back tubes as would be expected from the retention volumes of these substances at the temperature observed and for tubes of this geometry/flow range.[3] Concentration differences fall generally within the criteria stated above and do not show any consistent progression with increasing air volume.

Benzene and methylbenzene do not quite fit the criteria. One 6-liter sample is low for both. Those results, however, would be quite sensitive to the significant and especially variable blank correction for these two substances. One 54-liter sample gives high results for both. It should be least sensitive to inadequate blank corrections and no clear reason can be supplied. Nonetheless, the general agreement in the set over a range of volume of a factor of 9 is good for this technique. From a quality assurance perspective this approach added little except cost in this case.

Data in Table III span a range of air volumes only one-fourth as large but show strikingly different behavior. The evident decrease in apparent concentrations as air volume increases is large in most cases. Unlike Table II these values have not had the blank values shown subtracted. But, subtraction cannot alter the pattern of results.

Trichloroethene results are acceptable. The expected retention volume of 1,1,1-trichloroethane is about 15 liters at the temperature observed.[3] Therefore, actual loss by elution is a reasonable explanation for the lower

concentrations at the two larger volumes. Discarding the two higher volume results is reasonable. The remaining results are consistent giving presumptive evidence of describing the air sampled.

Benzaldehyde is considered an artifact.[2,3] It is always observed and generally behaves erratically at modest air volumes. It was included here in this one case just to illustrate that behavior. Those results tell nothing about atmospheric content of benzaldehyde.

No explanation about the strange aromatic hydrocarbon results is certain. Although implications of these data are clear from a quality assurance perspective, i.e., they cannot describe atmospheric content acceptably, it is difficult to imagine how that would have been discovered by conventional quality assurance activities.

Table IV displays results from two sets of tandem cartridges obtained at another location in another season. These data suggest again the presence of unidentified factors which would not be uncovered by the more conventional quality assurance checks. Benzene and methylbenzene display peculiar behavior. The concentrations from the front tubes are not acceptably constant. Concentrations from the back tubes do not behave as would be expected if simple elution loss were the only process occurring. In that case, the concentration from the front tube would decrease and that from the back increase as air volumes became larger. The sum of the two concentrations would be constant over the set until two retention volumes had been sampled. Although it is impossible to rule out some elution loss if a radical decrease in retention volumes due to atmospheric composition is not rejected, the pattern of results suggests another process operating as well. Although no definite mechanisms can be suggested artifact reactions seem likely. Benzene and methylbenzene have been reported as artifact products of clean Tenax in chemically simple situations.[7]

Dimethylbenzene exhibits borderline behavior, but disturbingly apparent concentrations decrease monotonically with increasing air volume. Other species are acceptably behaved. However, the modest amounts observed occasionally on the back tube suggest some presumably minor complication. Thus, it is important to note that acceptably constant values over a set do not guarantee data accuracy. Any process which scales linearly with air volume, e.g., perhaps some artifact mechanisms, and certainly any nonquantitative recovery upon desorption which is independent of surface coverage, will not be revealed by this approach.

Conclusions

Solid adsorbent sampling using a distributed air volume approach provides a small set of values which are sensitive to a large number of procedural and chemical variables. Costs are increased principally because of the increased analytical burden. However, some data presented here reveal in a straightforward way the operation of unidentified processes which have a significant effect on data quality. It is difficult to imagine how they might have been revealed by the usual quality assurance activities of either taking duplicate samples or duplicate tandem samples even if doped with isotopically altered species of interest, or of checking sampling and laboratory performance in the usual ways. In each situation there were some acceptable data. Generalizations are not apparent. Therefore, situation-specific indicators seem important. Distributed air volume sets seem capable of making a practical contribution to that end.

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TABLE II. Duplicate Sampling Experiment, Tenax Adsorbent
(Net $\mu g/m^3$)

Air Volume, (liters)	6		11		27		54		Blank (ng)
Substance/Sample	1	2	1	2	1	2	1	2	
Benzene	5.8	7.2	6.4	7.9	6.7	7.6	6.9	8.5	39
Methylbenzene	10.0	12.4	12.4	12.1	11.0	13.4	11.3	14.0	18
1,2-Dimethyl-benzene	2.8	3.7	3.4	3.2	2.6	3.3	2.8	3.5	
1,3,5-Trimethyl-benzene		0.78	0.87	0.78	0.66	1.11	0.84	1.31	
Ethylbenzene	2.0	2.6	2.5	2.3	2.0	2.5	2.1	2.8	4
Ethenylbenzene	0.55	0.63	0.55	0.56	0.46	0.61	0.47	0.52	6

Tubes were all tandem.
Nothing exceeding blank observed on back tubes.

TABLE III. Apparent Concentrations, Tenax Adsorbent
(Gross $\mu g/m^3$)

Substance	Air Volume (liters) 10	15	21	26	Blank (ng)
Benzene	8.83	7.04	3.65	4.41	10
Methylbenzene	17.36	15.71	11.60	10.04	5
1,2-Dimethylbenzene	3.91	3.48	3.32	2.37	
Ethylbenzene	6.21	4.36	3.26	2.33	
Ethenylbenzene	2.15	1.31	0.97	0.62	
Trichloroethylene	1.13	1.43	0.48	0.89	
1,1,1-Trichloroethane	3.24	3.15	1.39	1.97	
Benzaldehyde	10.89	3.63	6.26	1.59	30

TABLE IV. Tenax Adsorbent
Net Apparent Atmospheric Concentrations, $\mu g/m^3$

DATE
4/5

Volume, liters	6		11.4		26.9		54
Tube Position*	F	B	F	B	F	B	F
Substance							
Benzene	8.8	5.1	5.6	1.3	5.1	0.8	4.4
Methylbenzene	15.5	5.3	9.9	1.1	10.9	1.2	9.8
Dimethylbenzene	—	—	3.2	—	2.5	—	2.1
Trichloroethene	0.3	0.2	0.3	—	0.2	0.1	0.2
Tetrachloroethene	1.8	—	1.6	0.3	1.5	—	1.5

DATE
4/8

Volume, liters	6		11.4		26.9		54
Tube Position*	F	B	F	B	F	B	F
Substance							
Benzene	17.1	2.6	15.9	1.9	15.6	0.9	13.4
Methylbenzene	122	9.9	126	6.9	22.6	1.8	10.4
Dimethylbenzene	9.6	—	9.3	—	8.5	—	8.3
Trichloroethene	3.4	—	3.3	0.3	3.3	—	3.0
Tetrachloroethene	38.4	0.9	35.8	0.5	34.9	0.2	35.1

* Tandem Tubes Were Used for 3/4 of the Volumes
F = Front Tube
B = Backup Tube

KEYWORDS

Tenax

Air Sampling

Solid Adsorbents

Trace Organic Sampling

Distributed Air Volume Sets